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(54) Title: BLEACHING PROCESS FOR THE PRODUCTION OF HIGH BRIGHT PULPS

(57) Abstract

A process for the bleaching of mechanical and chemimechanical pulps which includes the steps of treating in a first stage the pulp with a reducing agent and subsequently treating the same pulp with a peroxygen compound in a second stage followed by a subsequent treatment with a peroxygen compound in a third stage.

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BLEACHING PROCESS FOR THE PRODUCTION OF HIGH BRIGHT PULPS

This invention relates to a multistage bleaching process in which reducing agents and oxidizing agents are used sequentially to bleach mechanical and chemimechanical pulps to high brightness levels and partially remove their yellow shade.

It is well recognized by those skilled in the art of mechanical and chemimechanical pulping that the quality of mechanical and chemimechanical pulps need to be improved in terms of brightness levels, color or yellowness and rapid reversion characteristics which occur with yellowing. Therefore various processes are currently employed in the pulp and paper industry to bleach these pulps for their use in a wide variety of paper products. The oldest process uses a reducing agent such as dithionite or sodium and zinc hydrosulfite (H) to brighten or bleach the pulps. With this bleaching chemical moderate gains of 4 to 10 points are obtained. Maximum brightness levels of 68 to 70% iso can be reached with the addition of approximately 1% to 1.25% on o.d. pulp of sodium hydrosulfite. The process is usually carried out in an aqueous phase at 3 to 5% consistency, a pH of 4.5 to 6.0, a temperature of about 60°C and a retention time of up to one hour. The use of a chelating or sequestering agent such as sodium tripolyphosphate (STPP) to remove naturally occuring trace metals is recommended. This agent is being added to the pulp prior to the addition of the reducing agent or is incorporated in the bleaching solution.

Today, peroxide (P) is the most commonly employed oxidizing agent for bleaching mechanical and chemimechanical pulps. This alkaline process is normally carried out in a single stage or in a double stage. In both cases, the bleaching is done at a pulp consistency of 15 to 35%, moderate temperatures of 50 to 70°C, and retention times of 2 to 3 hours for each

stage. In peroxide bleaching, stabilizers such as sodium silicate and magnesium sulfate are added to the bleach liquor to prevent decomposition of the oxidizing agent. Sodium hydroxide is also used to maintain an alkaline pH of 9.5 to 11 so as to increase the concentration of the perhydroxyl ion OOH^- which is beleived to be the active bleaching agent. Furthermore, pulps are normally pretreated at low consistency with organic chelating agents such as sodium diethylenetriamine penta-acetate (DTPA) to remove naturally occuring trace metals. Additional quantities are added in the bleach liquor to complex trace metals that are desorbed from the pulp as a result of the reaction of the bleaching agents with the chromophores of the pulp. In the bleaching of commercial pulps, iso brightness of 74-76% are conventionally achieved using this process with 3% hydrogen peroxide on o.d. pulp in a single stage while values of 76-78% iso-brightness are achieved in two stages in which greater retention times and higher peroxide charge are applied, i.e. 5% hydrogen peroxide on o.d. pulp.

Two stage bleaching of groundwood pulp using peroxide in the first stage and hydrosulfite (dithionite) in the second stage is well known and applied commercially (PH). An ISO-brightness level of 75-77% is achieved. However, much lower brightness levels are achieved when this two stage sequence is reversed (HP) (Schroter, H., Wbl. Papriefabr. 97, No. 23/24 (1969) p. 1023 and Joyce, P. and Mackie, M., CPPA, TAPPI International Pulp Bleaching Conference, Toronto, Canada, June 11-14, 1979, Preprint Page 116).

Other multistage bleaching processes have been disclosed in the literature but have not found commercial application. For instance, Loras, V. and Soteland, N. have published results for a three stage

bleaching sequence utilizing borohydride, peroxide and dithionite sequentially (BPH). This sequence was reported to yield a brightness of 88% from an initial level of 67%, an increase of 21 points. (High Brightness Bleaching of Mechanical Pulp, Norsk Skogindustri, 10/72 p. 255). It is also known from U.S. Patent 3,100,732 to Smedberg to use a combined and simultaneous action of an oxidizing agent and a reducing agent; the patentee also discloses that when using a double stage sequence, one uses the oxidizing agent first and subsequently the reducing agent. Liebergott, N., and Heitner, C. disclosed a multistage process for bleaching high yield and ultra-high yield pulps in which the pulp is treated sequentially with a peroxygen compound (P), a reducing compound (R) and a final peroxygen compound (P) to achieve higher brightness levels (Eur. Pat. Appl. EP 187,477). Tibbling, P. also disclosed a multiperoxide stage mechanical pulp bleaching process in which the pulp is treated sequentially with hydrogen peroxide in a first stage (P) and a second stages (P) and sodium hydrosulfite in a third stage (H) (Eur. Pat. Appl. EP 191,756). It is claimed that higher brightness levels are obtained than for those obtained for the bleaching sequence involving hydrogen peroxide (P) followed by sodium hydrosulfite (H).

It is an object of the present invention to provide a multistage bleaching process for mechanical and chemimechanical pulps which gives high brightness levels to such pulps and partially remove their yellow shade.

According to the present invention, there is provided a method for the bleaching of high yield or ultra high yield pulp which comprises the steps of sequentially treating the lignocellulosic fibres with

a reducing compound and subsequently treating the same fibres with peroxide in two successive stages.

In greater detail, the method or process includes three stages where the wood pulp is subjected to bleaching operations. The wood pulp which may be utilized is any high yield or ultra yield pulp such as mechanical, chemimechanical, chemithermomechanical, groundwood, refiner mechanical pulp, thermomechanical pulp, high yield and ultra high yield sulfite pulps.

In the first stage, the wood pulp is treated with a reducing compound which may be chosen from many such reducing compounds known to those skilled in the art. During this first stage, preferred reaction conditions include:

(1) a reducing compound charge of about 0.01 to about 1.5% by weight of oven dried pulp;
(2) the presence of a chelating agent such as DTPA or STPP;
(3) a reaction temperature of from about 60°C to 100°C;
(4) a reaction time of from about 4 to about 120 minutes;
(5) a pulp consistency of from 3% to about 35% and
(6) a reaction terminating pH of about 3.5 to about 11.0.

In the second stage, the pulp is bleached with a peroxygen compound. Preferred conditions of bleaching include:

(1) a peroxygen compound charge of about 0.1% to about 5% by weight of oven dried pulp in the presence of sodium hydroxide, sodium silicate, magnesium sulfate and DTPA;
(2) a reaction temperature of between about 60°C to about 100°C;

(3) a reaction time of from about 4 minutes to about 180 minutes;

(4) a pulp consistency of from about 4% to about 40%; and

(5) a reaction terminating pH of from about 8.5 to about 10.5.

In the third and final bleaching stage a peroxygen compound is utilized which is similar to the one used in the second stage. The preferred reaction conditions include:

(1) a peroxygen compound charge of about 0.1% to about 12.0% in the presence of sodium hydroxide, sodium silicate, magnesium sulfate and DTPA;

(2) a reaction temperature of from about 60°C to about 100°C;

(3) a reaction time of about 4 minutes to about 240 minutes;

(4) a pulp consistency of from about 4% to about 40%; and

(5) a reaction terminating pH from about 7.5 to about 10.0.

The compounds utilized in the process of the present invention may be selected from among these well known to those skilled in the art. Thus, the reducing compounds may be chosen from commercially inorganic reducing agents such as sodium or zinc hydrosulfite (dithionite), sodium or magnesium bisulfite, sodium borohydride, Borol* (a solution of sodium borohydride and sodium hydroxide), thiourea dioxide, ammonium borohydride, hydrazine and organic reducing agents such as amine-boranes and phosphine-boranes. It will be noted that some of these reducing agents are sold commercially with a chelating agent mixed therewith.

*Registered Trade Mark

Examples of the peroxide compound utilized in the second and third stages may include conventional inorganic peroxides such as hydrogen and sodium peroxide and also organic peroxides such as benzyl peroxide, ditertiary-butyl peroxide and peracetic acid.

The process flow diagram of figure 1 illustrates the various steps of a continuous operation in which pulps are bleached in multistage according to the present invention. In the process the pulp is first washed with a dewatering device (1) such as, but not exclusively, a standard screw press, a displacement washing screw press, a twin wire press, a disc filter or a twin roll press. These devices allow for water removal from the pulp slurry as well as for washing of contaminants such as sodium sulfite, metal ions, organic extractives, dissolved solids, etc., which are known to impair on the bleaching reactions between the bleaching agents and lignocellulosic fibres. Following this washing stage the pulp is mixed with the bleaching liquor containing the reducing agent. Mixing devices (2) such as single or double shaft mixers, refiner type mixers, high shear mixers and medium or low consistency pumps can be used. It is important in this stage of the process to disperse the bleaching liquor uniformly onto the fibre surface so that bleaching reactions can prevail over darkening reactions that also occur when lignocellulosic fibres are submitted to high temperature. After this pulp mixing stage the reducing agent reacts with the pulp in an upflow tower or steaming tube (3). A chemical charge of 0.75 to 1.25% sodium hydrosulfite and of 0.3 to 0.5% of sodium borohydride by weight of oven dried pulp are the preferred charges. A temperature between 65 to 85^{o}C; a consistency between 3.5 to 5% for sodium hydrosulfite and of 10 to 12% for sodium borohydride; a reaction time of between 1 to 40 minutes is

preferred at this stage to favor a more effective use of the reducing agent as it cannot be reused in the system. A reaction terminating pH of about 4.5 to 5.0 for sodium hydrosulfite and of about 10.0 to 10.5 for sodium borohydride is also recommended. Following this first stage bleaching with a reducing agent the pulp is dewatered and washed with a dewatering device (4) such as those described previously and used in position (1). The purpose is to wash the unreacted reducing agents or byproducts produced from the bleaching reactions so as to minimize its carry over to the next bleaching stage. After this pressing and washing stage the pulp is mixed with the peroxide bleaching liquor in a mixer (5). Other devices such as those described previously and used in position (2) can also be used. The efficiency of the mixer is important at this stage of the process to disperse the bleaching liquor uniformly onto the fibre surface so that oxidizing bleaching reactions of the chromophoric groups on the lignocellulosic fibres occur and prevail over darkening reactions that also occur when pulps are submitted to high temperatures. We show in figure 1 a mixer (5) which allows for the addition of steam and the peroxide bleaching liquor simultaneously. Following this mixing stage the pulp is transferred to a bleaching tower (6). The most preferred charge of the peroxygen compound in this second stage bleaching is in amount equal to the charge of the last bleaching tower or to one third of the charge of the last bleaching tower. Sodium hydroxide, sodium silicate and magnesium sulfate are preferably added in charge ranges of 0.5-3.0%, 0.0 to 3.0% and 0.01-0.05% respectively. It is also preferable to add small amounts of DTPA between 0.1-0.4%. All these components stabilize the peroxygen compound, in the form of the perhydroxyl ion, initiate and maintain a stable bleaching reaction. In a commercial operation the peroxide bleaching liquor mixed with the pulp at this

stage can be either prepared from fresh commercial components dissolved in water in separate tanks or it can be a residual bleaching liquor solution from the last stage bleaching tower (9). We have found from mass balance calculations that this latter is preferable to minimize the operating and bleaching cost of the process disclosed in this application. The size of the second bleaching tower (6) is to be determined considering the production rate, reaction time and pulp consistency selected or desired. We have found that a consistency in the 10-12% range, a retention time of 60 to 90 minutes and a temperature of 65 to 70°C are preferable to minimize the bleaching cost of the process disclosed. In figure 1 we show a schematic of a tower which is discharged with a medium consistency pump so as to have an operation with an efficient control over the bleaching conditions.

Following this second stage bleaching with an oxidizing agent the pulp is dewatered and washed with a dewatering device (7) such as those described previously and used in position (1) and (4). The purpose is to wash the byproducts produced from the bleaching reactions which occured in the second stage bleaching tower, avoid their carry over to the next bleaching stage and eliminate these from the bleach plant with an adequate white water recirculation strategy. After this pressing and washing stage the pulp is mixed with the peroxide bleaching liquor in a mixer (8). The mixer used and its efficiency are important at this stage for the same reasons as those elaborated previously above. Following this mixing stage the pulp is transferred to a bleaching tower (9). The preferred charge of the peroxygen compound in this third stage bleaching is 3 to 10% by weight of oven dried pulps. Sodium hydroxide, sodium silicate and magnesium sulfate are preferably added in charge ranges of 0.25-0.3%, 0.01% to 3.0% and 0.01-0.05%

respectively. It is also preferable to add small amounts of DTPA between 0.2-0.4%. In a commercial operation it is preferable in this last bleaching stage that fresh peroxide bleaching liquor be used and mixed with the pulp. This bleaching liquor is normally prepared from fresh commercial components which are dissolved in water in separate tanks. In addition to this fresh liquor, a small quantity of the residual bleaching liquor solution from the same tower (9) can also be used. The residual bleaching liquor is recovered with the last pair of dewatering presses (11 and 12). We have found that high charges of peroxide are required in this last bleaching tower to achieve high brightness levels. The size of the third bleaching tower (9) is to be determined considering the production rate, reaction time and pulp consistency selected or desired. We have found that a consistency in the 20-35% range is preferable to have high effective concentrations of the oxidizing agents so as to minimize the bleaching cost of the process disclosed.

In figure 1 we show a schematic of a tower which is discharged in a transfer chest (10) with a screw conveyer. This device allows for a positive displacement out of the tower so as to provide an efficient control over the operating and bleaching conditions of the pulp in the tower.

Following this third stage bleaching with an oxidizing agent the pulp is washed and dewatered with dewatering devices, (11) and (12), such as those described previously. At this stage it is important to add fresh water in the transfer chest (10) to wash the pulp by dilution and minimize brightness reversion subsequently. After the final stage of the bleaching process the pulp is pressed so as to recover the unreacted peroxide bleaching liquor and to reuse it in

the process as shown in figure 1. This white-water recirculation strategy and counter current washing lowers the operating cost of the bleaching process disclosed. The addition of sulfuric acid in the transfer chest (10) or the addition of SO_2 in the fluffer (13) is also desirable to lower the aqueous solution pH to about 6 to minimize brightness reversion subsequently.

Having thus generally described the invention, reference will be made to the following examples;

EXAMPLE 1.

A commercial spruce balsam chemithermomechanical pulp from an Eastern Canadian mill was washed with 0.5% diethylenetriaminepentaacetate (DTPA) for 30 minutes at 60°C and 3% consistency to eliminate metal ions which impair the bleaching reactions. Following this treatment, the pulp was pressed to 25% consistency and bleached. The experimental conditions and chemical charges are given in Table 1.

The bleaching chemicals were mixed by hand with a 20-g pulp sample, while the pulp consistency was simultaneously adjusted with demineralized water. Subsequently, the bags were sealed and immersed in a thermostatically controlled bath for the bleaching reactions to occur. After bleaching, the pulps were neutralized to destroy the bleaching agents and to adjust the pulp pH to minimize brightness reversion. For hydrogen peroxide bleaching, sodium metabisulfide was used, while sulfuric acid was used for the other bleaching agents.

The pulps were neutralized by diluting the pulp to 3% consistency with the neutralizing agent, mixing the slurry for 5 minutes, and pressing the pulp to 18% consistency. After neutralization, two samples of 3.5g

each were used to make the handsheets. The pulps were disintegrated for 2 minutes at a consistency of approximately 0.3%. The sheets were made with demineralized water on a British handsheet machine following the procedures prescribed by the Canadian Pulp and Paper Association. The sheets were pressed for 2 minutes at 50 psig and dried for 24 h at 23°C and 50% RH. The brightness was measured with an Elrepho spectrophotometer. Reflectance measurements with Filter Nos. 8, 9, 10, and 11 were made and used to calculate the color coordinates (CIE LAB) reference system. ISO brightness reported are the reflectance values at 457 nm using filter No. 8.

In the multistage bleaching experiments, each stage was similar to the single stage. However, the two-stage experiments were carried out with 30-g pulp samples, and 40-g samples were used for three stages. In all cases, a 7-g sample was taken at the end of each stage and was processed to obtain brightness values.

The results in Table I show the superiority of the multistage bleaching process disclosed in the present invention compared to the bleaching processes which constitute the prior art. High brightness values are achieved (ISO-brightness and L*) and a great deal of the yellow shade of the pulps is removed (B* values) while the pulps have less greenish shade than those bleached with peroxide only (P). These benefits remain after reversion. It can also be observed that for the bleaching process disclosed less peroxide is consumed to achieve higher brightness levels.

EXAMPLE 2.

A commercial spruce balsam chemithermomechanical pulp was pretreated and bleached following the experimental procedures described in example 1 and under the chemical charges and bleaching conditions given in Table 2. The results in Table 2 show the superiority of the multistage bleaching process disclosed in the present invention compared to other multistage bleaching sequences; peroxide-reducing agent-peroxide (PRP) and peroxide-peroxide-sodium hydrosulfite (PPH). With the sequences sodium hydrosulfite-peroxide-peroxide (HPP) and sodium borohydride-peroxide-peroxide (BPP) higher ISO-brightness values are obtained for a given total peroxide addition level while less peroxide is consumed in the process. Inversely at a constant peroxide consumption level lower ISO-brightness values are obtained with the bleaching procedures of the prior art compared with the process disclosed in this application. In addition to higher brightness values it can be seen from Table 2 that low B* values are obtained which indicate that the pulp bleached following the process disclosed is less yellow than the control pulp, as well as the pulp bleached with hydrogen peroxide only or upon bleaching with the procedures described in the prior art.

EXAMPLE 3.

A commercial spruce balsam chemithermomechanical pulp was pretreated and bleached following the experimental procedures described in example 1. In this series of experiments the pulp was bleached under different charges of the reducing agent in the first stage. The charges used were from 0.01% to 0.5% while the total peroxide charge was kept constant at 5%. The

results in Table 3 show that higher brightness values are obtained with increasing charges of the reducing agent. It can be observed that an optimum charge between 0.1 to 0.3% is desirable. Progressively lower B* values are obtained with the addition of the reducing agent therefore eliminating a great deal of the yellowness of the pulp.

EXAMPLE 4.

A commercial spruce balsam chemithermomechanical pulp was pretreated and bleached following the experimental procedures described in example 1. In this series of experiments the pulp was bleached under a given charge of 0.3% of the reducing agent, sodium borohydride, in the first stage while increasing charges of peroxide up to 5% by weight on oven dried pulp were added in the second and third stages. The results in Table 4 show that higher brightness values are obtained with increasing charges of peroxide in the second and third stages. It can be observed that small brightness gains are realized with charge levels slightly in excess of 3% so that preferred conditions would be for an addition level of 4 to 5% in peroxide o.d. weight when sodium borohydride is used. Progressively lower B* values are obtained with the addition of peroxide therefore eliminating a great deal of the yellowness of the pulp.

EXAMPLE 5.

A commercial spruce balsam chemithermomechanical pulp was pretreated and bleached following the experimental procedures described in example 1. In this series of experiments the pulp was bleached using a constant charge of 0.5% sodium hydrosulfite as the

reducing agent in the first stage. In the second and third stages progressively increasing peroxide charges were added from 1% to 8% o.d. weight o.d. pulp. The results in Table 5 show that higher brightness values are obtained with increasing charges of peroxide in the second and third stages. It can be observed that smooth increases are obtained up to 8% added peroxide allowing for high brightness levels and appreciable pulp yellowness removal.

EXAMPLE 6.

A commercial spruce balsam chemithermomechanical pulp was pretreated and bleached following the experimental procedures described in example 1. In this series of experiments the pulp was bleached using a constant charge of 1.0% sodium hydrosulfite as the reducing agent in the first stage. In the second and third stages progressively increasing charges of peroxide were added from 1% to 8% o.d. weight on pulp. The results in Table 5 show that higher brightness values are obtained with increasing charges of peroxide in the second and third stages. It can be observed that smooth increases are obtained up to 8% added peroxide allowing for high brightness levels and appreciable pulp yellowness removal. It can be appreciated that higher brightness levels are achieved compared to example 5 so that preferred reducing agent charges are 1.0 to 1.25% o.d. weight on pulp.

It will be understood that the above described embodiments are for purposes of illustration only and that changes and modifications may be made thereto without departing from the spirit and scope of the invention.

TABLE 1: BLEACHING CHEMICALS AND SEQUENCES

CHEMICAL CHARGES AND BLEACHING CONDITIONS		UNBL. PULP	HYDRO-SULFITE (H)	PEROXIDE (P)	PEROXIDE-HYDROSULFITE (PH)	(PH)	PEROXIDE (PP)	BLEACHING PROCESS DISCLOSED (HPP)	(HPP)	(EPP)	(BPP)
FIRST STAGE											
Na2SiO3	%		-	3.00	3.00	3.00	3.00	-	-	-	-
MgSO4	%		-	0.05	0.05	0.05	0.05	-	-	-	-
NaOH	%		-	3.00	1.60	1.00	1.00	-	-	-	-
D.T.P.A.	%		0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40
H2O2 ADDED	%		-	3.00	2.50	4.00	2.50	-	-	-	-
NaBH4	%		-	-	-	-	-	-	-	0.30	0.30
Na2S2O4	%		1.00	-	-	-		1.00	1.00	-	-
CONSISTENCY	%		5.0	15.0	10.0	10.0	10.0	5.0	5.0	10.0	10.0
TEMPERATURE	C		70	70	70	70	70	70	70	70	70
RETENTION TIME	min.		30	90	90	90	90	30	30	20	20
pH (INITIAL)	-		5.5	11.0	11.0	11.0	11.0	5.4	5.3	11.7	11.5
pH (FINAL)	-		5.0	9.6	8.4	8.5	9.5	4.9	5.0	10.4	10.4
SECOND STAGE											
Na2SiO3	%				-	-	3.00	3.00	3.00	3.00	3.00
MgSO4	%				-	-	0.05	0.05	0.05	0.05	0.05
NaOH	%				-	-	1.54	1.74	2.26	1.33	1.39
D.T.P.A.	%				0.40	0.40	0.40	0.40	0.40	0.40	0.40
H2O2 ADDED	%				-	-	2.50	2.50	4.00	1.50	2.50
Na2S2O4	%				1.00	1.00	-	-	-	-	-
CONSISTENCY	%				5.0	5.0	20.0	10.0	10.0	10.0	10.0
TEMPERATURE	C				70	70	70	70	70	70	70
RETENTION TIME	min.				30	30	90	90	90	90	90
pH (INITIAL)	-				5.4	5.4	11.0	10.9	10.0	11.1	11.0
pH (FINAL)	-				4.2	4.4	10.7	8.7	8.0	10.1	10.5
THIRD STAGE											
Na2SiO3	%							3.00	3.00	3.00	3.00
MgSO4	%							0.05	0.05	0.05	0.05
NaOH	%							1.75	2.00	1.00	1.00
D.T.P.A.	%							0.40	0.40	0.40	0.40
H2O2 ADDED	%							2.50	4.00	1.50	2.50
CONSISTENCY	%							20.0	20.0	20.0	20.0
TEMPERATURE	C							70	70	70	70
RETENTION TIME	min.							90	90	90	90
pH (INITIAL)	-							11.1	11.1	11.1	11.1
pH (FINAL)	-							10.5	10.6	10.5	10.5
TOTAL											
H2O2 (ADDED)	%			3.00	2.50	4.00	5.00	5.00	8.00	3.00	5.00
H2O2 (RESIDUAL)	%			0.79	1.32	2.46	2.18	2.79	5.56	1.66	2.85
H2O2 (CONSUMED)	%			2.21	1.18	1.54	2.82	2.21	2.44	1.34	2.15
OPTICAL PROPERTIES											
BEFORE REVERSION :											
BRIGHTNESS (ISO-457nm)	%	62.5	68.5	77.1	76.4	77.4	78.5	79.0	80.5	77.0	78.2
L*	-	88.1	91.4	95.1	94.5	94.8	95.3	95.0	95.3	95.1	95.0
A*	-	-0.37	-0.98	-2.16	-1.88	-1.95	-2.66	-1.97	-2.03	-2.67	-2.28
B*	-	9.25	9.68	9.16	8.61	8.48	8.33	7.49	6.68	8.35	7.98
AFTER REVERSION :											
BRIGHTNESS (ISO-457nm)	%	61.9	67.5	75.7	74.5	75.0	76.6	77.7	78.4	75.5	77.0
L*	-	88.0	91.1	94.5	94.2	94.2	94.4	94.0	95.0	94.0	94.1
A*	-	-0.37	-1.14	-3.00	-1.94	-1.75	-3.00	-1.00	-2.01	-2.72	-2.70
B*	-	9.64	10.00	9.10	9.40	8.90	7.03	8.00	7.50	8.92	7.39

TABLE 2:

CHEMICAL CHARGES AND BLEACHING CONDITIONS		UNBL. PULP	BLEACHING CHEMICALS AND SEQUENCE — BLEACHING PROCESS DISCLOSED											
			(PP)	(PP)	(PBP)	(PBP)	(PHP)	(PHP)	(PPH)	(PPH)	(BPP)	(BPP)	(HPP)	(HPP)
FIRST STAGE														
Na2SiO3	%		3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	-	-	-	-
MgSO4	%		0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	-	0.00	-	-
NaOH	%		1.00	1.00	1.50	1.50	1.50	1.50	1.00	1.00	1.00	1.00	-	-
D.T.P.A.	%		0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40
H2O2 ADDED	%		2.50	1.52	2.50	-	2.50		2.50	-	-	-	-	-
NaBH4	%		-	-	-	-	-	-	-	-	0.30	0.30	-	-
Na2S2O4	%		-	-	-	-	-	-	-	-	-	-	0.50	0.50
CONSISTENCY	%		10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	5.0	5.0
TEMPERATURE	C		70	70	70	70	70	70	70	70	70	70	70	70
RETENTION TIME	min.		90	90	90	90	90	90	90	90	20	20	30	30
pH (INITIAL)	-		11.0	11.0	11.0	11.0	11.0	11.0	11.0	11.0	11.5	11.5	5.4	5.2
pH (FINAL)	-		9.5	9.5	8.6	8.6	8.4	8.4	8.7	8.7	10.4	10.4	5.2	5.4
SECOND STAGE														
Na2SiO3	%		3.00	3.00	-	-	-	-	3.00	3.00	3.00	3.00	3.00	3.00
MgSO4	%		0.05	0.05	-	-	-	-	0.05	0.05	0.05	0.05	0.05	0.05
NaOH	%		1.54	1.54	1.00	1.00	-	-	1.70	1.70	1.39	1.39	1.74	1.74
D.T.P.A.	%		0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40
H2O2 ADDED	%		2.50	1.53	-	1.72	-	1.72	2.50	1.85	2.50	2.27	2.50	2.25
NaBH4	%		-	-	0.30	0.30	-	-	-	-	-	-	-	-
Na2S2O4	%		-	-	-	-	0.50	0.50	-	-	-	-	-	-
CONSISTENCY	%		20.0	20.0	10.0	10.0	5.0	5.0	20.0	20.0	10.0	10.0	10.0	10.0
TEMPERATURE	C		70	70	70	70	70	70	70	70	70	70	70	70
RETENTION TIME	min.		90	90	20	20	30	30	90	90	90	90	90	90
pH (INITIAL)	-		11.0	11.0	12.2	12.2	5.4	5.4	11.0	11.0	11.0	11.0	11.1	11.1
pH (FINAL)	-		10.7	10.7	11.0	11.0	4.4	4.4	10.3	10.3	10.5	10.5	8.6	8.6
THIRD STAGE														
Na2SiO3	%				3.00	3.00	3.00	3.00	-	-	3.00	3.00	3.00	3.00
MgSO4	%				0.05	0.05	0.05	0.05	-	-	0.05	0.05	0.05	0.05
NaOH	%				1.25	1.25	1.00	1.00	-	-	1.00	1.00	1.75	1.75
D.T.P.A.	%				0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40
H2O2 ADDED	%				2.50	1.73	2.50	1.73	-	1.85	2.50	2.32	2.50	2.25
Na2S2O4	%				-	-	-	-	0.50	0.50	-	0.28	-	-
CONSISTENCY	%				20.0	20.0	20.0	20.0	5.0	5.0	20.0	20.0	20.0	20.0
TEMPERATURE	C				70	70	70	70	70	70	70	70	70	70
RETENTION TIME	min.				90	90	90	90	30	30	90	90	90	90
pH (INITIAL)	-				11.0	11.0	11.0	11.0	5.5	5.5	11.1	11.1	11.0	11.0
pH (FINAL)	-				11.0	11.0	9.6	9.6	5.5	5.5	10.5	10.5	10.4	10.4
TOTAL														
H2O2 (ADDED)	%		5.00	3.05	5.00	3.45	5.00	3.45	5.00	3.70	5.00	4.55	5.00	4.50
H2O2 (RESIDUAL)	%		2.10	0.95	2.43	1.45	2.62	1.45	2.57	1.70	2.05	2.55	2.97	2.50
H2O2 (CONSUMED)	%		2.02	2.00	2.57	2.00	2.30	2.00	2.43	2.00	2.15	2.00	2.03	2.00
OPTICAL PROPERTIES														
BEFORE REVERSION :														
BRIGHTNESS (ISO-457nm)	%	52.0	70.5	75.9	79.0	70.9	77.5	76.7	70.0	77.0	70.2	70.2	70.9	70.7
L*	-	07.3	05.3	04.6	04.9	05.0	04.0	04.7	04.9	04.4	05.0	05.2	05.2	05.1
A*	-	-0.74	-2.05	-2.00	-1.05	-1.90	-2.02	-1.90	-1.91	-1.75	-2.20	-2.00	-2.00	-2.30
B*	-	0.37	0.33	0.17	7.20	0.10	0.25	0.00	7.99	0.25	7.90	7.00	0.02	0.00
AFTER REVERSION :														
BRIGHTNESS (ISO-457nm)	%	01.9	70.0	74.0	77.2	-	75.3	-	70.9	-	77.0	-	70.2	-
L*	-	07.4	04.4	03.0	03.7	-	04.4	-	04.7	-	04.1	-	05.1	-
A*	-	-1.25	-3.00	-3.10	-2.10	-	-1.70	-	-1.05	-	-2.70	-	-1.03	-
B*	-	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		[illegible]		[illegible]		[illegible]	

TABLE 3: CHEMICAL CHARGES AND BLEACHING CONDITIONS FOR THE SEQUENCE SODIUM BOROHYDRIDE-PEROXIDE-PEROXIDE (BPP)

FIRST STAGE								
NaOH	%		0.83	0.10	0.17	0.33	1.00	1.67
D.T.P.A.	%		0.40	0.40	0.40	0.40	0.40	0.40
NaBH4	%		0.01	0.03	0.05	0.10	0.30	0.50
CONSISTENCY	%		10.0	10.0	10.0	10.0	10.0	10.0
TEMPERATURE	C		70	70	70	70	70	70
RETENTION TIME	min.		20	20	20	20	20	20
pH (INITIAL)	-		8.3	9.7	10.3	10.9	11.5	11.8
pH (FINAL)	-		7.0	9.1	9.3	9.0	10.4	11.0
SECOND STAGE								
Na2SiO3	%		3.00	3.00	3.00	3.00	3.00	3.00
MgSO4	%		0.05	0.05	0.05	0.05	0.05	0.05
NaOH	%		1.74	2.09	1.56	1.39	1.39	1.22
D.T.P.A.	%		0.40	0.40	0.40	0.40	0.40	0.40
H2O2 ADDED	%		2.50	2.50	2.50	2.50	2.50	2.50
CONSISTENCY	%		10.0	10.0	10.0	10.0	10.0	10.0
TEMPERATURE	C		70	70	70	70	70	70
RETENTION TIME	hr.		1.5	1.5	1.5	1.5	1.5	1.5
pH (INITIAL)	-		11.0	11.0	11.0	11.0	11.0	11.0
pH (FINAL)	-		9.1	0.0	9.6	9.5	10.5	10.2
THIRD STAGE								
Na2SiO3	%		3.00	3.00	3.00	3.00	3.00	3.00
MgSO4	%		0.05	0.05	0.05	0.05	0.05	0.05
NaOH	%		1.25	1.00	0.75	1.25	1.00	1.00
D.T.P.A.	%		0.40	0.40	0.40	0.40	0.40	0.40
H2O2 ADDED	%		2.50	2.50	2.50	2.50	2.50	2.50
CONSISTENCY	%		20.0	20.0	20.0	20.0	20.0	20.0
TEMPERATURE	C		70	70	70	70	70	70
RETENTION TIME	hr.		1.5	1.5	1.5	1.5	1.5	1.5
pH (INITIAL)	-		11.1	11.0	11.0	11.2	11.1	11.0
pH (FINAL)	-		10.1	10.3	10.4	10.5	10.5	10.6
TOTAL								
H2O2 (ADDED)	%		5.00	5.00	5.00	5.00	5.00	5.00
H2O2 (RESIDUAL)	%		2.30	2.34	2.41	2.40	2.05	3.19
H2O2 (CONSUMED)	%		2.62	2.66	2.59	2.52	2.15	1.01
OPTICAL PROPERTIES								
BEFORE REVERSION :								
BRIGHTNESS (ISO-457nm)	%	62.0	77.5	77.2	77.0	70.5	70.2	77.0
L*	-	07.3	95.0	95.0	95.0	95.3	95.0	94.6
A*	-	-0.74	-2.71	-2.75	-2.75	-2.92	-2.20	-2.17
B*	-	0.37	0.77	0.54	0.52	0.25	7.90	7.64
AFTER REVERSION :								
BRIGHTNESS (ISO-457nm)	%	61.9	75.9	76.0	76.5	77.0	77.0	77.0
L*	-	07.4	94.1	94.1	94.1	94.1	94.1	93.0
A*	-	-1.25	-3.01	-3.01	-2.49	-2.93	-2.70	-2.42
B*	-	0.73	0.19	0.19	7.39	7.39	7.39	6.94

TABLE 4: CHEMICAL CHARGES AND BLEACHING CONDITIONS FOR THE SEQUENCE SODIUM BOROHYDRIDE-PEROXIDE-PEROXIDE (BPP)

FIRST STAGE					
NaOH	%	1.00	1.00	1.00	1.00
D.T.P.A.	%	0.40	0.40	0.40	0.40
NaBH4	%	0.30	0.30	0.30	0.30
CONSISTENCY	%	10.0	10.0	10.0	10.0
TEMPERATURE	C	70	70	70	70
RETENTION TIME	min.	20	20	20	20
pH (INITIAL)	-	11.5	11.5	11.7	11.5
pH (FINAL)	-	10.0	10.3	10.4	10.4
SECOND STAGE					
Na2SiO3	%	3.00	3.00	3.00	3.00
MgSO4	%	0.05	0.05	0.05	0.05
NaOH	%	0.70	1.22	1.39	1.39
D.T.P.A.	%	0.40	0.40	0.40	0.40
H2O2 ADDED	%	0.50	1.00	1.50	2.50
CONSISTENCY	%	10.0	10.0	10.0	10.0
TEMPERATURE	C	70	70	70	70
RETENTION TIME	hr.	1.5	1.5	1.5	1.5
pH (INITIAL)	-	11.0	11.0	11.1	11.0
pH (FINAL)	-	10.0	10.1	10.1	10.3
THIRD STAGE					
Na2SiO3	%	3.00	3.00	3.00	3.00
MgSO4	%	0.05	0.05	0.05	0.05
NaOH	%	1.15	1.50	1.00	1.00
D.T.P.A.	%	0.40	0.40	0.40	0.40
H2O2 ADDED	%	0.50	1.00	1.50	2.50
CONSISTENCY	%	10.0	10.0	10.0	10.0
TEMPERATURE	C	70	70	70	70
RETENTION TIME	hr.	1.5	1.5	1.5	1.5
pH (INITIAL)	-	11.1	11.0	11.1	11.1
pH (FINAL)	-	10.7	10.7	10.5	10.5
TOTAL					
H2O2 (ADDED)	%	1.00	2.00	3.00	5.00
H2O2 (RESIDUAL)	%	-	0.90	1.66	2.85
H2O2 (CONSUMED)	%	-	1.10	1.34	2.15
OPTICAL PROPERTIES					
BEFORE REVERSION :					
BRIGHTNESS (ISO-457nm)	%	62.0	74.3	76.9	77.0	78.2
L*	-	87.3	94.2	94.6	95.1	95.0
A*	-	-0.74	-2.42	-2.51	-2.67	-2.20
B*	-	8.37	9.48	8.68	8.35	7.98
AFTER REVERSION :					
BRIGHTNESS (ISO-457nm)	%	61.9	73.3	75.1	76.5	77.0
L*	-	87.4	93.5	93.9	94.0	94.1
A*	-	-1.25	-3.01	-2.69	-2.72	-2.78
B*	-	8.73	9.20	8.47	8.00	7.39

TABLE 5: CHEMICAL CHARGES AND BLEACHING CONDITIONS FOR THE SEQUENCE SODIUM HYDROSULFITE-PEROXIDE-PEROXIDE (HPP)

FIRST STAGE							
D.T.P.A.	%		0.40	0.40	0.40	0.40	0.40
Na2S2O4	%		0.50	0.50	0.50	0.50	0.50
CONSISTENCY	%		5.0	5.0	5.0	5.0	5.0
TEMPERATURE	C		70	70	70	70	70
RETENTION TIME	hr.		0.5	0.5	0.5	0.5	0.5
pH (INITIAL)	-		5.4	5.4	5.5	5.4	5.2
pH (FINAL)	-		4.0	4.5	4.7	5.2	5.1
SECOND STAGE							
Na2SiO3	%		3.00	3.00	3.00	3.00	3.00
MgSO4	%		0.05	0.05	0.05	0.05	0.05
NaOH	%		0.70	1.22	1.39	1.74	2.09
D.T.P.A.	%		0.40	0.40	0.40	0.40	0.40
H2O2 ADDED	%		0.50	1.00	1.50	2.50	4.00
CONSISTENCY	%		10.0	10.0	10.0	10.0	10.0
TEMPERATURE	C		70	70	70	70	70
RETENTION TIME	hr.		1.5	1.5	1.5	1.5	1.5
pH (INITIAL)	-		10.9	11.0	11.0	11.1	11.0
pH (FINAL)	-		9.7	8.7	8.5	8.6	8.0
THIRD STAGE							
Na2SiO3	%		3.00	3.00	3.00	3.00	3.00
MgSO4	%		0.05	0.05	0.05	0.05	0.05
NaOH	%		0.75	1.25	1.50	1.75	2.00
D.T.P.A.	%		0.40	0.40	0.40	0.40	0.40
H2O2 ADDED	%		0.50	1.00	1.50	2.50	4.00
CONSISTENCY	%		10.0	10.0	10.0	10.0	10.0
TEMPERATURE	C		70	70	70	70	70
RETENTION TIME	hr.		1.5	1.5	1.5	1.5	1.5
pH (INITIAL)	-		11.0	11.0	11.0	11.0	11.0
pH (FINAL)	-		10.3	9.0	9.0	10.4	10.0
TOTAL							
H2O2 (ADDED)	%		1.00	2.00	3.00	5.00	8.00
H2O2 (RESIDUAL)	%		0.26	0.70	1.45	2.97	4.45
H2O2 (CONSUMED)	%		0.74	1.22	1.55	2.03	3.55
OPTICAL PROPERTIES							
BEFORE REVERSION :							
BRIGHTNESS (ISO-457nm)	%	62.5	71.7	75.7	77	78.9	79.6
L*	-	88.1	93.7	94.5	94.9	95.2	95.0
A*	-	-8.37	-1.85	-2.15	-2.31	-2.00	-1.02
B*	-	9.23	10.91	9.10	8.07	8.02	6.07
AFTER REVERSION :							
BRIGHTNESS (ISO-457nm)	%	61.9	71.3	74.7	76.2	78.2	78.2
L*	-	88.0	93.5	94.4	94.7	95.1	94.9
A*	-	-0.37	-2.19	-2.38	-1.81	-1.93	-1.72
B*	-	9.64	11.36	9.69	9.06	8.03	7.60

TABLE 6: CHEMICAL CHARGES AND BLEACHING CONDITIONS FOR THE SEQUENCE SODIUM HYDROSULFITE-PEROXIDE-PEROXIDE (HPP)

FIRST STAGE							
D.T.P.A.	%		0.40	0.40	0.40	0.40	0.40
Na2S2O4	%		1.00	1.00	1.00	1.00	1.00
CONSISTENCY	%		5.0	5.0	5.0	5.0	5.0
TEMPERATURE	C		70	70	70	70	70
RETENTION TIME	hr.		0.5	0.5	0.5	0.5	0.5
pH (INITIAL)	-		5.4	5.5	5.4	5.4	5.3
pH (FINAL)	-		5.1	5.1	5.0	4.9	5.0
SECOND STAGE							
Na2SiO3	%		3.00	3.00	3.00	3.00	3.00
MgSO4	%		0.05	0.05	0.05	0.05	0.05
NaOH	%		1.39	1.39	1.57	1.74	2.25
D.T.P.A.	%		0.40	0.40	0.40	0.40	0.40
H2O2 ADDED	%		0.50	1.00	1.50	2.50	4.00
CONSISTENCY	%		10.0	10.0	10.0	10.0	10.0
TEMPERATURE	C		70	70	70	70	70
RETENTION TIME	hr.		1.5	1.5	1.5	1.5	1.5
pH (INITIAL)	-		11.1	11.0	11.0	10.9	10.0
pH (FINAL)	-		9.5	9.1	9.0	0.7	0.0
THIRD STAGE							
Na2SiO3	%		3.00	3.00	3.00	3.00	3.00
MgSO4	%		0.05	0.05	0.05	0.05	0.05
NaOH	%		1.00	1.25	1.25	1.75	2.00
D.T.P.A.	%		0.40	0.40	0.40	0.40	0.40
H2O2 ADDED	%		0.50	1.00	1.50	2.50	4.00
CONSISTENCY	%		20.0	20.0	20.0	20.0	20.0
TEMPERATURE	C		70	70	70	70	70
RETENTION TIME	hr.		1.5	1.5	1.5	1.5	1.5
pH (INITIAL)	-		11.1	11.0	10.9	11.1	11.1
pH (FINAL)	-		10.2	10.2	9.9	10.5	10.6
TOTAL							
H2O2 (ADDED)	%		1.00	2.00	3.00	5.00	8.00
H2O2 (RESIDUAL)	%		0.19	0.81	1.60	2.79	5.56
H2O2 (CONSUMED)	%		0.81	1.19	1.40	2.21	2.44
OPTICAL PROPERTIES							
BEFORE REVERSION :							
BRIGHTNESS (ISO-457nm)	%	62.5	71.4	75.7	76.0	79.0	80.5
L*	-	00.1	93.4	94.5	94.5	95.0	95.3
A*	-	-0.37	-2.00	-1.05	-1.66	-1.97	-2.03
B*	-	9.25	10.01	9.17	0.45	7.49	6.60
AFTER REVERSION :							
BRIGHTNESS (ISO-457nm)	%	61.9	70.4	74.7	75.7	77.7	70.4
L*	-	00.0	93.1	94.4	94.4	94.0	95.0
A*	-	-0.37	-1.07	-1.93	-1.59	-1.00	-2.01
B*	-	9.64	11.04	9.69	0.95	0.00	7.50

CLAIMS

1. A process for the bleaching of mechanical and chemimechanical pulps which includes the steps of treating in a first stage the pulp with a reducing agent and subsequently treating the same pulp with a peroxygen compound in a second stage followed by a subsequent treatment with a peroxygen compound in a third stage.

2. The process of claim 1 in which the reducing agent is sodium hydrosulfite.

3. The process of claim 2 in which treatment of the pulp in the first stage utilizes a chemical charge of 0.75 to 1.25% sodium hydrosulfite by weight of oven dried pulp in the presence of a chelating agent at a reaction temperature between 65 to 85^{o}C, a consistency between 3.5 to 5%, a reaction time between 1 and 40 minutes and a reaction terminating pH of about 4.5 to 5.0.

4. The process of claim 3 in which following the first stage bleaching with a reducing agent the pulp is dewatered and washed to remove unreacted reducing agents and by-products.

5. The process of claim 4 in which 3 to 10% of peroxygen by weight of oven dried pulp is dispersed into the pulp using a mixer and transferring the pulp and bleaching fluid to a bleaching tower.

6. The process of claim 5 in which sodium hydroxide, sodium silicate and magnesium sulfate are added to stabilize the peroxygen compound in ranges of 0.5 - 3.0%, 0.0 to 3.0% and 0.01 to 0.05% respectively.

7. The process of claim 6 in which small amounts of DTPA between 0.1 - 0.4% are added to the bleach fluid.

8. The process of claim 7 in which the consistency of the pulp is in the 10 - 12% range, the temperature is 65 - 70°C and the retention time is 60 to 90 minutes.

9. The process of claim 8 in which the pulp from the first bleaching tower is dewatered and washed to remove the by-products produced from the bleaching reactions.

10. The process of claim 9 in which 3 to 10% of peroxygen by weight of oven dried pulp is dispersed into the pulp using a mixer and the pulp and bleaching fluid are transferred to a bleaching tower.

11. The process of claim 10 in which sodium hydroxide, sodium silicate and magnesium silicate are added to stabilize the peroxygen compound in ranges of 0.5 - 3.0%, 0.0 to 3.0% and 0.01 to 0.05% respectively.

12. The process of claim 11 in which the consistency of the pulp is in the range from 20 - 35%, and primarily fresh peroxygens are mixed with the pulp.

13. The process of claim 12 in which the pulp is washed and dewatered following the third stage bleaching.

14. The process of claim 13 in which sulfuric acid is added to the pulp after washing and dewatering to lower the aqueous solution pH to about 6.

15. The process of claim 1 in which the reducing agent is sodium borohydride.

16. The process of claim 15 in which treatment of the pulp in the first stage utilizes a chemical charge of 0.3 to 0.5% of sodium borohydride by weight of oven dried pulp in the presence of a chelating agent at a reaction temperature between 65 to 85°C, a consistency between 10 and 12%, a reaction time between 1 to 40 minutes and a reaction terminating pH of 10.0 to 10.5.

17. The process of claim 16 in which following the first stage bleaching with a reducing agent the pulp is dewatered and washed to remove unreacted reducing agents and by-products.

18. The process of claim 17 in which 3 to 10% of peroxygen by weight of oven dried pulp is dispersed into the pulp using a mixer and transferring the pulp and bleaching fluid to a bleaching tower.

19. The process of claim 18 in which sodium hydroxide, sodium silicate and magnesium sulfate are added to stabilize the peroxygen compound in ranges of 0.5 - 3.0%, 0.0 to 3.0% and 0.01 to 0.05% respectively.

20. The process of claim 19 in which small amounts of DTPA between 0.1 - 0.4% are added to the bleach fluid.

21. The process of claim 20 in which the consistency of the pulp is in the 10 - 12% range, the temperature is 65 - 70^{o}C and the retention time is 60 to 90 minutes.

22. The process of claim 21 in which the pulp from the second stage bleaching tower is dewatered and washed to remove the by-products produced from the bleaching reactions.

23. The process of claim 22 in which 3 to 10% of peroxygen by weight of oven dried pulp is dispersed into the pulp using a mixer and the pulp and bleaching fluid are transferred to a bleaching tower.

24. The process of claim 23 in which sodium hydroxide, sodium silicate and magnesium silicate are added to stabilize the peroxygen compound in ranges of 0.5 - 3.0%, 0.0 to 3.0% and 0.01 to 0.05% respectively.

25. The process of claim 24 in which the consistency of the pulp is in the range from 20 - 35%, and primarily fresh peroxygens are mixed with the pulp.

26. The process of claim 25 in which the pulp is washed and dewatered following the third stage bleaching.

27. The process of claim 26 in which sulfuric acid is added to the pulp after washing and dewatering to lower the aqueous solution pH to about 6.

28. The process of claim 1 characterized by the reducing compound being selected from the group consisting of sodium bisulfite, magnesium bisulfite, zinc hydrosulfite, BOROL, thiurea dioxide, ammonium borohydride and hydrazine.

29. The process of claim 1 in which the treatment of the pulp with the reducing agent utilizes a charge of about 0.01 to about 1.5% by weight in the presence of a chelating agent at a reaction temperature of between 60°C to 100°C for a time of between 4 to 120 minutes at a pulp consistency of from 3% to 35% and a reaction terminating pH of between 3.5 to about 11.0; the process being further characterized by washing said pulp after treatment.

30. The process of claim 29 characterized by the peroxygen compound being selected from the group consisting of hydrogen peroxide, sodium peroxide, benzyl peroxide, ditertiarybutyl peroxide and peracetic acid.

31. The process of claim 30 in which the treatment of the pulp with a peroxygen compound in the second stage utilizes a charge of between 0.01% to about 5.0% by weight at a temperature of between 60°C to 100°C for a time period of between 4 minutes to 180 minutes at a pulp consistency of between 4% to about 40% and a reaction terminating pH of between 0.5 to 10.5.

32. The process of claim 31 in which the treatment with said peroxygen compound in the third stage utilizes a charge of between 0.1 to about 12% by weight based on oven dried pulp at a temperature of between 60°C to 100°C

for a period of from 4 minutes to 250 minutes at a pulp consistency of between 4% and 40% and a reaction terminating pH of from 7.5 to about 10.0.

33. The process of claim 32 characterized by the peroxygen compounds being selected from the group consisting of sodium peroxide, benzyl peroxide, ditertiarybutyl peroxide and peracetic acid.

34. The process of claim 33 characterized by the treatment of the pulp with the peroxygen compounds being carried out in the presence of sodium hydroxide, sodium silicate, magnesium sulfate and DTPA.

35. The process of claim 1 characterized by the pulp being selected from the group of pulps consisting of high yield and ultra high yield pulps which are referred to as mechanical, chemimechanical, chemithermomechanical, groundwood, high-yield or ultra high yield sulfite pulps.

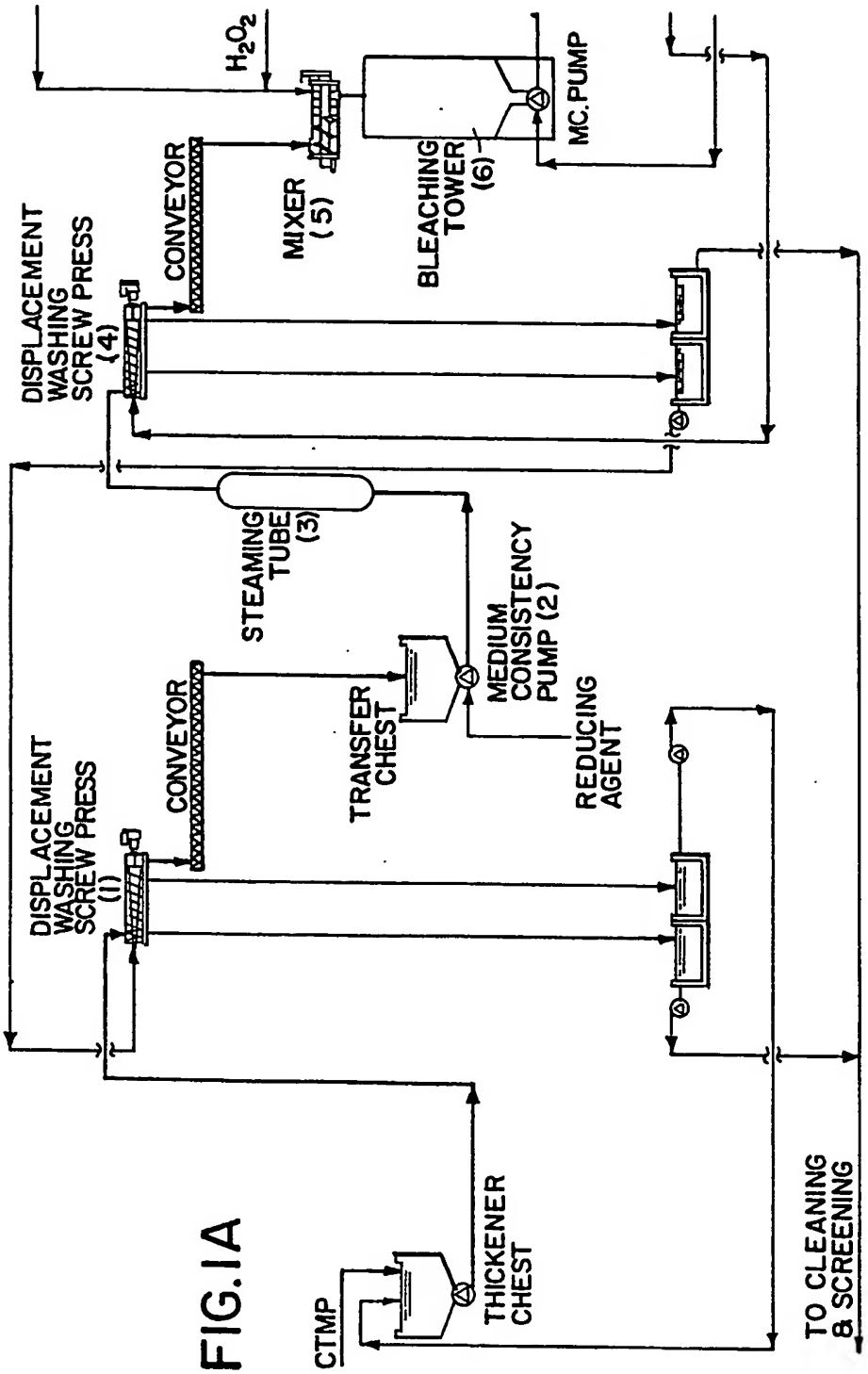
H_2O_2
MIXER (5)
BLEACHING TOWER (6)
MC. PUMP
CONVEYOR
DISPLACEMENT WASHING SCREW PRESS (4)
STEAMING TUBE (3)
MEDIUM CONSISTENCY PUMP (2)
TRANSFER CHEST
REDUCING AGENT
CONVEYOR
DISPLACEMENT WASHING SCREW PRESS (1)
THICKENER CHEST
CTMP
TO CLEANING & SCREENING

FIG. IA

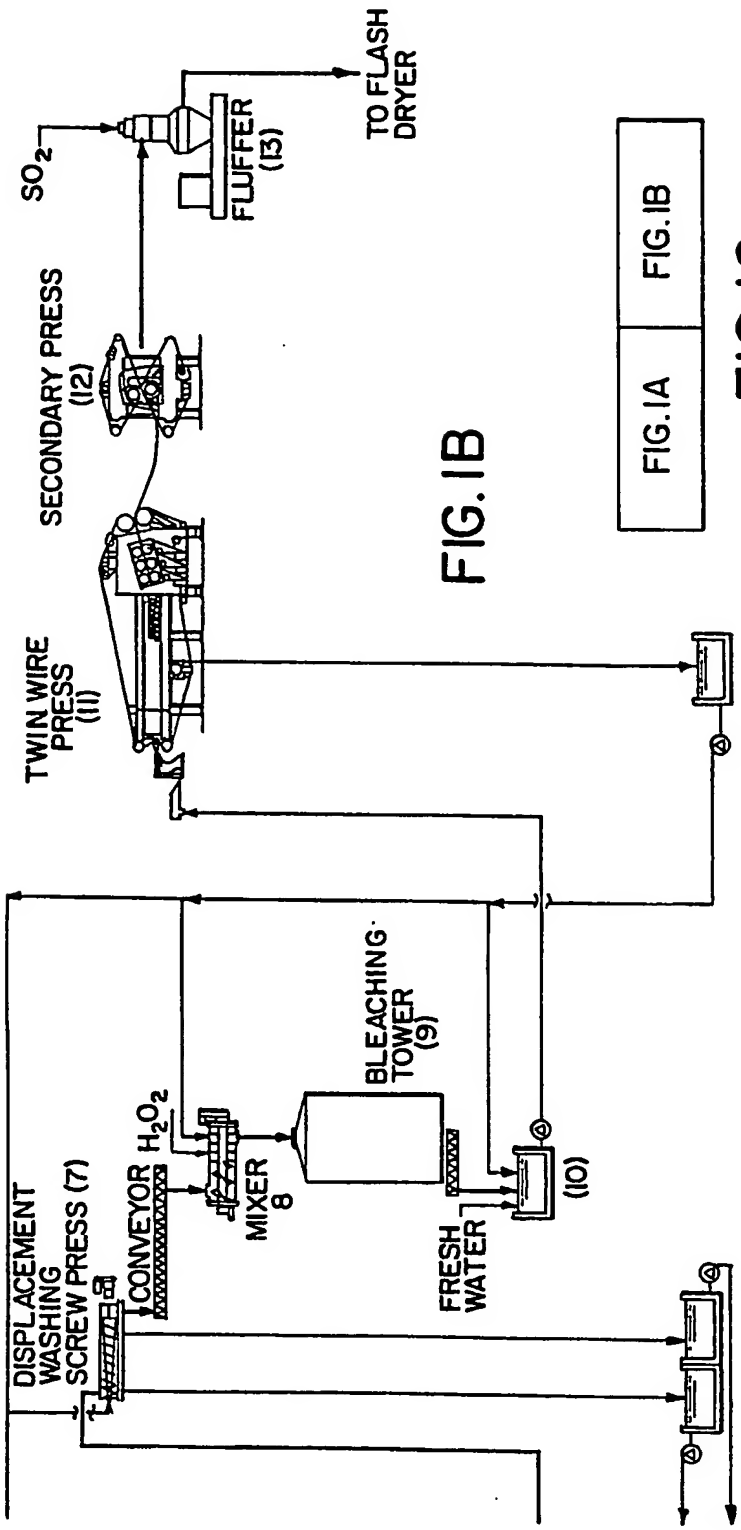

FIG. IB

FIG. IA | FIG. IB

FIG. IC

INTERNATIONAL SEARCH REPORT

International Application No PCT/CA 90/00097

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 D21C9/10

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	D21C

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
Y	EP,A,0187477 (PULP AND PAPER RESEARCH INSTITUTE OF CANADA) 16 July 1986 see the whole document (cited in the application)	1-11, 14-24, 27-35
Y	BULLETIN OF THE INSTITUTE OF PAPER CHEMISTRY. vol. 53, no. 2, August 1982, APPLETON US page 260 M.YOTSUYA et al.: "Peroxide bleaching of high-yield pulp." see the whole document	1-11, 14-24, 27-35
A	EP,A,0191756 (KAMYR AB) 20 August 1986 see the whole document (cited in the application)	

° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
20 JULY 1990	16 AOUT 1990
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	SONGY O.M-L.A.

Form PCT/ISA/210 (second sheet) (January 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

CA 90/00097
SA 35818

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 20/07/90

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		JP-A- 61186593	20-08-86
		US-A- 4804440	14-02-89
EP-A-0191756	20-08-86	JP-A- 61245392	31-10-86
		SE-A- 8600615	16-08-86